SCIENCE FOR CERAMIC PRODUCTION

UDC 666.324:536.4.002.3

SPECIFICS OF PHASE FORMATION IN REFRACTORY CLAY IN THE PRESENCE OF TOPAZ

T. V. Vakalova,[1] V. I. Vereshchagin,[1] O. A. Chernousova,[1] T. A. Khabas,[1] and V. M. Golovanov[1]

The processes of phase formation in refractory clay in the presence of topaz-bearing rock additives are investigated. It is established that the effect of topaz proper is determined by its quantity. Topaz in low quantities (up to 0.5 – 1.0%) intensifies the formation of primary and secondary mullite of prismatic habitus, lowers the temperature of mullite synthesis, and improves the mullite structure. An increase in the topaz content over 25% is accompanied by the formation of mullite of needle-shaped habitus, in addition to prismatic mullite.

The current goal of the domestic ceramic industry is the development of new materials, both by modification of existent mixtures and the involvement of nontraditional raw materials. Topaz is very promising in this respect. First, it is an insular fluoraluminosilicate that within the temperature interval of 850 – 1350°C fully transforms into mullite of needle-shaped habitus. Second, the volatile fluorides released in dissociation of topaz can be of practical interest as mineralizers in ceramic mixtures.

It was earlier established that the use of topaz rocks as grog components in aluminosilicate refractories instead of traditional chamotte results in a significant improvement of thermal-mechanical properties, and its use in porcelain mixtures lowers the sintering temperature and improves the whiteness of porcelain and some other functional characteristics [1 – 3]. Of special interest are studies of the effect of topaz additives on the phase processes occurring in heating of clay, especially on the mullite formation process, since mullite is the crystalline phase which to a large extent determines the properties of finished aluminosilicate ceramic articles. Not only the total content of mullite in ceramics, but its structural and morphological state as well are significant.

The clay component selected for the studies was a kaolinite variety of Troshkovskoe refractory clay, which is sufficiently well studied and used in production of fine ceramics, in particular, porcelain and faience, and in aluminosilicate refractories, mostly as the grog component. However, after special treatment, this clay can be successfully used as a binding agent. The characteristics of the Troshkovskoe clay are described in [4].

The topaz-bearing component was represented by two samples of topaz rocks from the Kopna deposit (Kemerovo Region), which have different material compositions and are hereafter designated as the quartz-topaz rock and the topaz ore.

The chemical and mineralogical compositions of the materials are given in Tables 1 and 2.

The first additive tested was quartz-topaz rock depleted in topaz, in which quartz prevailed over topaz (66.94 and 31.2%) and which was introduced in quantities ranging from 5 to 25% with a 5% interval. With this rock being the additive, quartz and fluorine components were introduced along with the topaz proper (Table 3).

TABLE 1

Raw material	Weight content, %					
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	calcination loss
Troshkovskoe clay*	50.09	36.49	2.54	0.96	0.39	9.01
Quartz-topaz rock	78.11	15.73	0.38	0.21	0.72	4.71**
Topaz ore	59.65	26.25	0.35	0.10	1.31	12.34**

* In addition, Troshkovskoe clay contained 0.52% R_2O.

** Calcination at 1350°C.

[1] Tomsk Polytechnic University, Tomsk, Russia; Urskoe Research and Production Association JSC, Novokuznetsk, Russia.

TABLE 2

Raw material	Content, %				
	kaolinite and halloysite	colloid minerals	free quartz	topaz	other minerals
Troshkovskoe clay	66.39	19.52	6.68	–	7.41
Quartz-topaz rock	–	–	66.94	31.24	1.86
Topaz ore	–	–	43.31	54.96	1.72

The preparation of the raw materials consisted in grinding to a dispersion of not more than 0.088 mm. The samples were molded by dry-press molding at the pressure 2.5 MPa. The firing was carried out at 1000, 1150, 1250, and 1350°C with at least 0.5 h exposure at the maximum temperature. The samples cooled freely together with the kiln.

The physicochemical processes occurring in the heat treatment of clay-topaz compositions were investigated using x-ray phase analysis and electron microscopy.

The analysis of the obtained dependences of the diffraction maximum intensities of the main crystalline phases on the content of added quartz-topaz rock at particular firing temperatures shows that the formation of new compounds (mullite and cristobalite) and transformation of quartz upon varying the additive concentrations proceed ambiguously (Fig. 1).

It was found that heating pure clay (hereafter understood as clay without additives) and mixtures of clay with additives, regardless of their ratio, to 1000°C was insufficient for the synthesis of mullite and cristobalite. The diffraction patterns of mixtures fired at 1000°C exhibit only intense quartz reflections. It should be noted that here and in all subsequent cases, the quartz content estimated by the intensity of the respective x-ray reflections represents its total content comprised by quartz introduced as the clay impurity, quartz introduced with the quartz-topaz rock less the quartz dissolving in the melt, and quartz undergoing polymorphous transformations.

An increase in the heating temperature to 1150°C sharply changes the diffraction patterns of the fired products. Along with the quartz reflections, intense mullite and cristobalite reflections emerge both in pure clay and in mixtures of clay and quartz-topaz rock.

The decrease in the intensity of quartz reflections at 1150°C in mixtures with each tested additive, as compared to 1000°C, is related both to the dissolution of quartz in the silicate melt and to transformation of quartz into cristobalite, which determines the appearance of cristobalite reflections on the respective diffraction patterns.

Furthermore, all analyzed mixtures at 1150 and 1250°C register more intense dissolution in the melt of primary mullite released from the kaolinite structure, compared to the initial clay (Fig. 1b, curves 2 and 3), which can be accounted for by modification of the flow and reaction properties of the
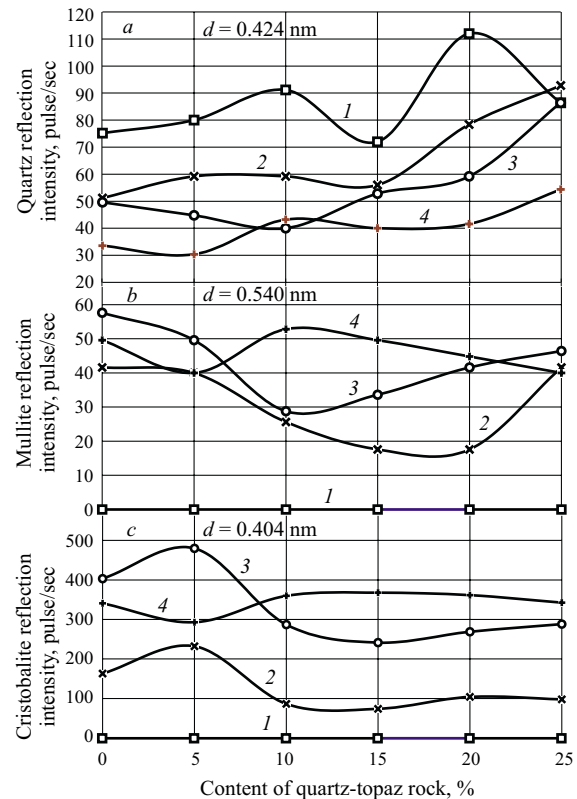

Fig. 1. Variations in x-ray reflection intensity of quartz (*a*), mullite (*b*), and cristobalite (*c*) depending on the quantity of quartz-topaz rock additive at firing temperatures of 1000 (*1*), 1150 (*2*), 1250 (*3*), and 1350°C (*4*).

melt under the effect of fluorides formed in the decomposition of topaz.

As for the specifics of cristobalite formation at 1150 and 1250°C, the diffraction maximum observed with a 5% additive of quartz-topaz rock is determined by intense cristobalitizing of amorphous silica as the product of decomposition of kaolinite and its crystallization in the silicate melt, which is formed in a sufficient quantity at these temperatures. The subsequent decrease in the intensity of cristobalite reflections while the introduced additive increases from 5 to 25% (Fig. 1c, curves 2 and 3) is presum-

TABLE 3

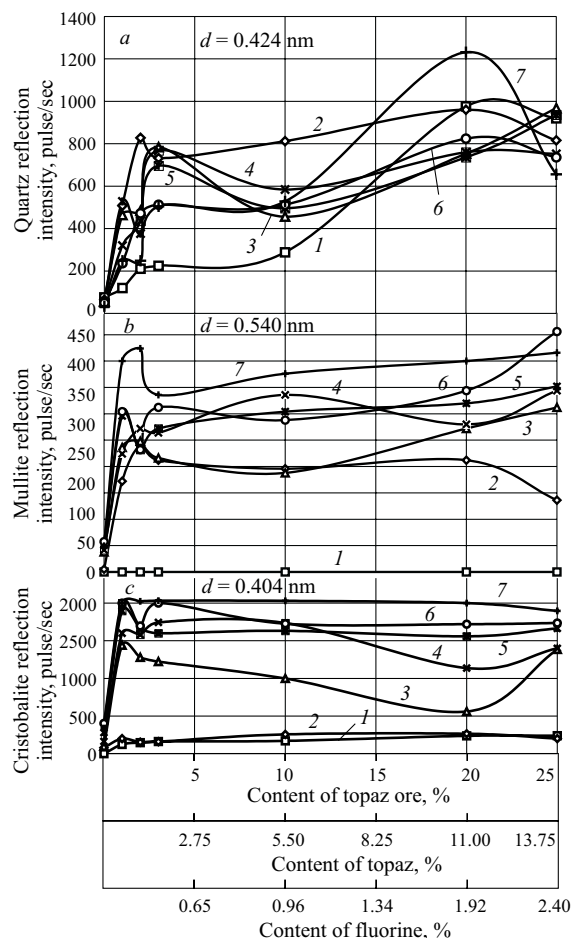| Content of additive, %	Content in quartz-topaz rock, %			Content in topaz ore, %		
	topaz	quartz	fluorine	topaz	quartz	fluorine
1	–	–	–	0.55	0.43	0.09
2	–	–	–	1.10	0.86	0.19
3	–	–	–	1.65	1.29	0.28
5	1.50	3.35	0.26	–	–	–
10	3.00	6.70	0.52	5.50	4.30	0.96
15	4.50	10.50	0.78	–	6.45	–
20	6.00	13.40	1.04	11.00	8.60	1.92
25	7.50	16.75	1.31	13.75	10.75	2.40

Fig. 2. Variations in x-ray reflection intensity of quartz (*a*), mullite (*b*), and cristobalite (*c*) depending on the quantity of topaz ore additive at firing temperatures of 1000 (*1*), 1050 (*2*), 1100 (*3*), 1150 (*4*), 1200 (*5*), 1250 (*6*), and 1350°C (*7*).

ably caused by the development of favorable conditions, which facilitate dissolving in the melt of cristobalite that is formed as a consequence of amorphous SiO_2 crystallization and transformation of quartz introduced with quartz-topaz rock (Table 3).

An increase in the temperature to 1350°C radically transforms the pattern of variation in the mullite and cristobalite reflections. A slight minimum at 5% additive observed on these dependence curves is presumably related to the dissolution of cristobalite and mullite in the low-viscosity silicate melt, whose decreased viscosity is presumably determined not only by the high heating temperature, but also by the effect of fluorides intensely released from the topaz structure.

A certain increase in the intensity of cristobalite reflections and their stabilization with an increasing content of additive (Fig. 1*c*, curve *4*) are caused by the increased content of introduced quartz and the prevalence of cristobalitizing of quartz over its dissolution.

Thus, the above findings of the experiment established the effect of quartz-topaz rock additive on the modifications

of phase transformations in refractory clay. However, as the selected temperature intervals were rather wide, with spacing of 100 – 150°C, and the additive content spacing was 5%, it was found expedient to carry out more detailed studies, in which the temperature interval was narrowed to 50°C, and the additive content was 1, 2, 3, 10, 20, and 25% (Table 3). Furthermore, based on the assumption that a sufficiently high content of the quartz component in the quartz-topaz rock (up to 67%) can affect the mullite formation process, the quartz-topaz rock in the experiment was replaced by topaz ore that is richer in topaz (up to 55% topaz and 43% quartz).

The preparation of raw materials, samples, and their heat treatment conditions were the same as in the previous experimental series.

Analysis of the resulting data indicated that mullite is registered in the initial clay without additive only beginning with the temperature 1100°C; moreover, the reflections of the emerging primary mullite have low intensity and are blurred, which is evidence of the imperfection of its crystalline structure (Fig. 2). In the same way, none of the mixtures of clay with topaz rock when fired at 1000°C produced mullite that could be identified by x-ray analysis. However, as soon as 1% additive was introduced, clearly resolved and highly intense mullite reflections were registered already at the temperature 1050°C, and the dependence of their intensity variation on the quantity of introduced additive (same as for other registered phases) is extremal, the maximum correlating to 1 – 2% topaz rock additive. This is presumably due to the mineralizing effect of topaz, whose mechanism is determined by the temperature conditions of synthesis. At low temperatures, the function of topaz is reduced to the formation of mullite seeds, which act as crystallization centers for the primary mullite formed from kaolinite, which activates this process and enhances the mullite yield.

As the firing temperature grows, and the processes of liquid-phase sintering evolve, accompanied by intense formation of silicate melt, the role of topaz changes, and the determining effect is caused by the gaseous fluorine compounds released in disintegration of the topaz structure, which decreases the melt viscosity and develops the favorable conditions for the dissolution of primary mullite formed from kaolinite and the recrystallization of secondary mullite. In the electron microscope photos of the products of firing at 1350°C of virtually all mixtures with a topaz rock content up to 20% (up to 11% topaz proper), mullite is represented by crystals of clear habitus and edging, mostly of the usual short-prismatic shape, the size ranging from 0.5 to 1 μm (Fig. 3*a*). It is only when the introduced additive quantity increases to 25% (14% converted to topaz, Table 3) that along with the prismatic mullite, the photos clearly register needle-shaped mullite with crystal size from 5 to 10 μm (up to 15 μm), which is formed in topaz decomposition (Fig. 3*b*).

The analysis of the variations of quartz reflection intensities depending on the heating temperature and the quantity of introduced additive (Fig. 2*a*) points to the ambiguity of the

transformation of the quartz component in the considered mixtures. Two extremums are seen in the curves virtually at all temperatures. The first extremum is related to the introduction of $1 - 2\%$ additive (depending on the temperature). The second is related to 20% additive of topaz rock. The significant increase in the intensity of quartz reflections at $1 - 2\%$ rock additive and heating from 1000 to 1150°C is probably due to the structural modifications in the crystal lattice of quartz present in the clay, under the effect of volatile fluorides as the products of topaz dissociation. A further increase in the temperature from 1150 to 1350°C is accompanied by a decrease in the quartz reflections, which may be caused by the partial transformation of quartz into metacristobalite or by the dissolution of quartz in the melt that is formed at these temperatures, or, most probably, by both of these processes simultaneously. The maximum registered with 20% topaz ore additive and heating from 1000 to 1150°C can be accounted for by the increased quartz amount introduced with the rock (approximately to 8.5%). The decrease in the intensity of quartz reflections in the mixture of this particular composition when heated from 1150 to 1350°C is caused by the transformation of the specified quartz component.

An introduction of topaz ore in refractory clay affects not only the process of mullite formation and quartz transformation, but the formation of cristobalite as well. Similar to the previous cases, such effect of the topaz additive depends on its quantity. Whereas cristobalite reflections are registered in clay without additives only at 1100°C, the presence of $1 - 2\%$ topaz rock ensures the formation of cristobalite already at 1000°C (Fig. 2c). A further increase in temperature from 1050 to 1350°C is accompanied by the abrupt acceleration of cristobalite formation, which, same as in the case of quartz, can be attributed to the activating effect of fluorine on the silica transformation process. Up to the temperature 1150°C, cristobalite is mainly formed through the crystallization of amorphous silica released in the dissociation of kaolinite. It is established that as the additive content increases from 2 to 20%, the dependences characterizing this process at 1000 and 1150°C monotonically decrease, which is evidence of partial dissolution of the formed cristobalite in the melt and subsequent crystallization. The stabilization of cristobalite intensity reflections in mixtures with additives from 2 to 25% at temperatures from 1200 to 1350°C is determined by the overall effect of the transformation of quartz introduced with clay and topaz ore.

In addition to determining the effect of topaz-bearing rock additives on the phase transformation in kaolinite, the effect of these additives on sintering of kaolinite clay was investigated as well.

The analysis of the effect of additives of quartz-topaz rock with the quartz content prevailing over topaz (67 and 31%, respectively) in an amount of 25% on the properties of Troshkovskoe clay indicated that this rock, regardless of the additive quantity and the temperature, has a negative effect on the consolidation and hardening process, which is mani-
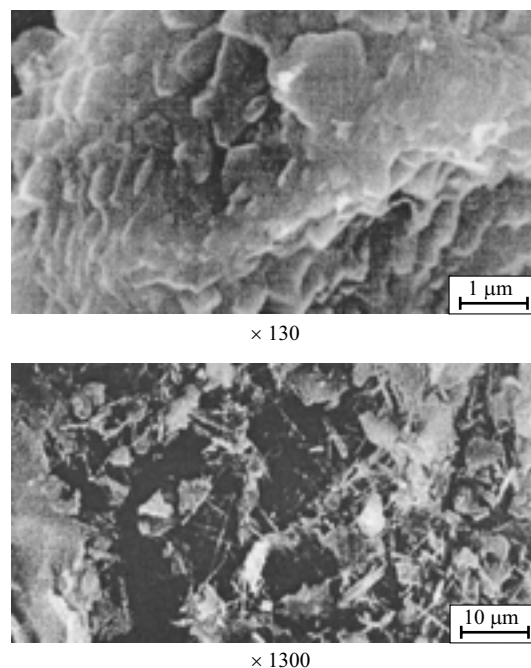

× 130

× 1300

Fig. 3. Microstructure of products of firing of Troshkovskoe clay with additives of 20% (*a*) and 25% (*b*) topaz ore at 1350°C.

fested in the nearly double increase in the porosity of the structure, depending on the particular additive and the temperature, and the $2 - 3$-fold decrease in the strength parameters, which is determined by the polymorphism of the quartz component introduced with the quartz-topaz rock.

As for the topaz rock that is richer in topaz proper than the quartz-topaz rock (55 and 30%, respectively), its effect on the sintering of kaolinite is determined by its quantity; in other words, the entire concentration range of the considered additives can be arbitrarily split into low quantities (from 1 to 3%) and large quantities (over 3%) of additives.

It is established that regardless of the quantity of additives, firing at 1000°C (before the start of clay sintering) significantly increases the porosity of the end material and decreases the linear shrinkage.

An increase in the temperature from 1000 to 1350°C sharply activates the process of sintering of mixtures with low quantities (up to 3%) of rock additives, accompanied by the regular increase in shrinkage, decreased water absorption, and increased strength, which is caused by the mineralizing effect of topaz on the formation of mullite and the effect of gaseous fluorine compounds on the flow and reaction properties of the emerging silicate melt.

The use of topaz ore additives in large quantities (over 3%) has the opposite effect on sintering, i.e., when fired at temperatures above 1000°C sintering deteriorates due to the increased content of introduced quartz and the activation of cristobalite formation.

Thus, the effect of topaz on sintering, phase transformations, composition, and some properties of refractory clay

heated within the temperature interval of 1000 – 1350°C has been investigated.

It is established that the effect of additives of topaz-bearing material depends on its mineralogical composition, namely, the ratio between topaz proper and quartz. The data on the retarding effect of an increased quartz content on mullite formation are corroborated.

The effect of topaz proper on the physicochemical processes in refractory clay is determined by its quantity. In small quantities (up to 0.5 – 1.0%), topaz intensifies the formation of mullite and cristobalite, which is accompanied by lowering the temperature of their synthesis by 50°C, an increased yield, and a more perfect structure of the mullite.

The dependence of the effect of additives of topaz-bearing materials on their mineralogical composition and concentration will determine the areas of practical application for these materials in mixtures with refractory clays.

Topaz-containing rock additives with an elevated topaz content (at least 50%) in low quantities (0.5 – 1.0% converted to topaz proper) are recommended for use in traditional technologies of clay-bearing ceramics, in particular, porcelain or aluminosilicate refractories with the usual chamotte grog component, whose functional properties can be improved due to the activation of sintering and mullite formation. It is known that released gaseous fluorine is partly (up to 50%) assimilated by glass or ceramic structure. Therefore, in the case of using up to 0.5 – 1% topaz additives, the presence of fluorine compounds in waste gases in an amount of 0.05 – 0.06 g/m^3 somewhat exceeds the maximum permissible concentration requirements. These waste gases require additional purification.

Topaz-bearing material used in large quantities is recommended as the main component in clay-bearing mixtures, where the role of clay is reduced to the binding ingredient in production of nontraditional ceramics, for instance, aluminosilicate refractories, in which the grog component totally consists of raw topaz material, or topaz material acts as an additive to the traditional chamotte component. The improved service qualities of the products of firing of kaolinite clay with an increased topaz content are due to the needle-shaped habitus of the emerging mullite crystals. In this case, fluorine, which is present in an amount of 5.5 – 6.0 g/m^3 in waste gases, should be extracted employing efficient refinement methods, which will make it possible to solve the environmental problem and at the same time increase the cost effectiveness of the process by converting fluorine into a valuable product (fluosilicic acid and various fluorides and silicofluorides).

REFERENCES

1. S. G. Dolgikh, A. K. Karklit, A. V. Kakhmurov, and S. A. Suvorov, "Topaz as a refractory material," *Ogneupory*, No. 7, 14 – 19 (1990).
2. T. V. Vakalova, V. I. Vereshchagin, T. A. Khabas, and O. A. Chernousova, "Prospects of using mineral raw materials from Siberian Region in refractory material technologies. Physical chemistry and technology of oxide silicate materials: Proceed. Int. Scien.-Tech. Conf. in Ekaterinburg," *Vestn. UGTU*, No. 1, 26 – 28 (2000).
3. V. M. Pogrebenkov, K. S. Kostikov, A. A. Reshetnikov, and V. M. Golovanov, "Topaz ore as a promising material in porcelain production," in: *Complex Industrial Development of the Kopna Deposit. Proceed. of All-Russia Scien.-Tech. Conf.* [in Russian], Kemerovo (1999), pp. 26 – 29.
4. T. V. Vakalova, "Kaolinic and plastic state of refractory clay from the Troshkovskoe deposit," *Steklo Keram.*, No. 11, 23 – 26 (1997).